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(54) Olefin polymerization catalyst and olefin polymerization process

Katalysator und Verfahren zur Olefinpolymerisation

Catalyseur et procédé pour la polymérisation d'oléfines

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Description

The present invention relates to an olefin polymerization catalyst comprising a metallocene compound, an organoaluminum compound, and a metal borate or aluminate, and a process for polymerizing olefin by use of the catalyst.

Various catalysts are known for olefin polymerization. JP-A-3-197513 discloses polymerization of ethylene by use of a metallocene compound and an organoaluminum compound as the catalyst. JP-A-3-290408 discloses a process for producing polyethylene or ethylene copolymer by use of a zirconocene compound, an organoaluminum compound, and an organomagnesium compound as the catalyst. These catalysts, however, are not satisfactory in activity in polymerization of propylene although they are useful for production of polyethylene and ethylene copolymers.

Further, JP-A-58-19309 and other papers disclose processes of polymerization of olefin including propylene with a catalyst constituted of a metallocene compound and methylaluminoxane with high activity. This catalyst system has disadvantages of high cost of the methylaluminoxane and residual aluminum in the formed polymer because a relatively large amount of the methylaluminoxane needs to be used. JP-A-3-207704 discloses a highly active catalyst for polymerization of olefin including propylene: the catalyst composed of an ionic metallocene is activated by addition of an organoaluminum compound. The ionic metallocene, the main catalyst, is generally prepared by reaction of a metallocene compound with an ionizing ionic compound. The ionizing ionic compound for preparing the ionic metallocene catalyst is synthesized by converting a metal borate or a metal aluminate into an ammonium salt or a triphenylcarbenium salt. Therefore, this catalyst system has disadvantages that synthesis of the ionizing ionic compound requires many steps of operations and involves many problems on the purity thereof, reproducibility in the synthesis, deactivation during storage and on transfer to a polymerization vessel, and so forth.

EP-A-0 513 380 discloses a process for producing an olefin based polymer wherein homopolymerization of an α -olefin or copolymerization of α -olefins is carried out in the presence of a catalyst comprising as main components:

(A) a transition metal compound

(B) a compound capable of forming an ionic complex when reacted with a transition metal compound, and

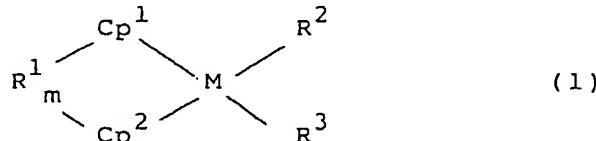
(C) an organoaluminium compound.

The inventors of the present invention made comprehensive investigation to solve the above problems, and found that olefin is polymerized with a catalyst formed from a metallocene compound, an organoaluminum compound, and a metal borate or aluminate, which is to be converted to the ionizing ionic compound, with high catalyst activity to produce polyolefin of high moldability.

The present invention intends to provide a catalyst for polymerization of olefin formed from the components of a metallocene compound, an organoaluminum compound, and a metal borate or aluminate.

The present invention also intends to provide a process of polymerization of olefin with the above catalyst.

The catalyst for polymerization of olefin of the present invention comprises (A) a metallocene compound, (B) an organoaluminum compound, and (C) a metal borate or a metal aluminate: the metallocene compound (A) being represented by the general formula (1) below:



45 where Cp^1 and Cp^2 are independently a substituted or unsubstituted cyclopentadienyl group; R^1 is an alkylene group, an arylalkylene group, dialkylsilylene group, dialkylgermylene group, an alkylphosphinediyl group, or an alkylimino group having 1 to 20 carbons, R^1 crosslinking Cp^1 and Cp^2 together; m is 0 or 1; M is titanium, zirconium, or hafnium; and R^2 and R^3 are independently hydrogen, halogen, or a hydrocarbon group, an alkoxy group, or an aryloxy group having 1 to 12 carbons, the organoaluminum compound (B) being represented by the general formula (2) below:



where each R^4 is independently hydrogen, an alkyl group, an alkoxy group, or an aryl group, at least one R^4 being an

alkyl group, and
the metal borate or the metal aluminate (C) being represented by the general formula (3):

5 $(C(L)_n)_b(A)_d$ (3)

where C is an alkali metal cation or an alkaline earth metal cation; L is a Lewis base; A is an anion having elemental boron or elemental aluminum; n is an integer of from 1 to 6; b and d are respectively an integer selected to balance the electric charge.

10 The process of polymerization of olefin of the present invention is conducted by use of the above catalyst.

The metallocene compound employed in the present invention is represented by the general formula (1) above.

The specific examples of the metallocene include :

15 bis(cyclopentadienyl)zirconiumdimethyl,
bis(methylcyclopentadienyl)zirconiumdimethyl,
bis(butylcyclopentadienyl)zirconiumdimethyl,
ethylenebis(indenyl)zirconiumdimethyl,
isopropylidene(cyclopentadienyl-1-fluorenyl)zirconiumdimethyl,
20 dimethylsilylbis(2,4,5-trimethylcyclopentadienyl)zirconiumdimethyl,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconiumdimethyl,
dimethylsilylbis(3-methylcyclopentadienyl)zirconiumdimethyl,
bis(cyclopentadienyl)zirconium dichloride,
bis(methylcyclopentadienyl)zirconium dichloride,
25 bis(butylcyclopentadienyl)zirconium dichloride,
ethylenebis(indenyl)zirconium dichloride,
isopropylidene(cyclopentadienyl-1-fluorenyl)zirconium dichloride,
dimethylsilylbis(2,4,5-trimethylcyclopentadienyl)zirconium dichloride,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconium dichloride,
30 dimethylsilylbis(3-methylcyclopentadienyl)zirconium dichloride,
bis(cyclopentadienyl)zirconiumdiphenyl,
bis(methylcyclopentadienyl)zirconiumdiphenyl,
bis(butylcyclopentadienyl)zirconiumdiphenyl,
ethylenebis(indenyl)zirconiumdiphenyl,
35 isopropylidene(cyclopentadienyl-1-fluorenyl)zirconiumdiphenyl,
dimethylsilylbis(2,4,5-trimethylcyclopentadienyl)zirconiumdiphenyl,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconiumdiphenyl,
dimethylsilylbis(3-methylcyclopentadienyl)zirconiumdiphenyl,
bis(cyclopentadienyl)zirconiumdibenzyl,
40 bis(methylcyclopentadienyl)zirconiumdibenzyl,
ethylenebis(indenyl)zirconiumdibenzyl,
isopropylidene(cyclopentadienyl-1-fluorenyl)zirconiumdibenzyl,
dimethylsilylbis(2,4,5-trimethylcyclopentadienyl)zirconiumdibenzyl,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)zirconiumdibenzyl,
45 dimethylsilylbis(3-methylcyclopentadienyl)zirconiumdibenzyl,
bis(cyclopentadienyl)methoxyzirconium monochloride,
bis(methylcyclopentadienyl)methoxyzirconium monochloride,
bis(butylcyclopentadienyl)methoxyzirconium monochloride,
ethylenebis(indenyl)methoxyzirconium monochloride,
50 isopropylidene(cyclopentadienyl-1-fluorenyl)methoxyzirconium monochloride,
dimethylsilylbis(2,4,5-trimethylcyclopentadienyl)methoxyzirconium monochloride,
dimethylsilylbis(2,4-dimethylcyclopentadienyl)methoxyzirconium monochloride,
dimethylsilylbis(3-methylcyclopentadienyl)methoxyzirconium monochloride,
bis(cyclopentadienyl)methylzirconium monochloride,
55 bis(methylcyclopentadienyl)methylzirconium monochloride,
bis(butylcyclopentadienyl)methylzirconium monochloride, ethylenebis(indenyl)methylzirconium monochloride,
isopropylidene(cyclopentadienyl-1-bis(cyclopentadienyl)methylzirconium monochloride,

dimethylsilylbis(2,4,5-trimethylcyclopentadienyl)methylzirconium monochloride, dimethylsilylbis(2,4-dimethylcyclopentadienyl)methylzirconium monochloride, dimethylsilylbis(3-methylcyclopentadienyl)methylzirconium monochloride; and metallocene compounds derived by replacing the zirconium in the above zirconium compounds with titanium, or hafnium.

5 The organoaluminum compound (B) is represented by the general formula (2) above. The specific examples of the organoaluminum compound include :

10 trimethylaluminum, triethylaluminum, triisopropylaluminum, tri(n-propyl)aluminum, triisobutylaluminum, tri(n-butyl)aluminum, triamylaluminum, dimethylaluminum ethoxide, diethylaluminum ethoxide, diisopropylaluminum ethoxide, di(n-propyl)aluminum ethoxide, diisobutylaluminum ethoxide, di(n-butyl)aluminum ethoxide, dimethylaluminum hydride, diethylaluminum hydride, diisopropylaluminum hydride, di(n-propyl)aluminum hydride diisobutylaluminum hydride, di(n-butyl)aluminum hydride.

15 20 The metal borate or the metal aluminate (C) is represented by the general formula (3) above. The specific examples of ether and tetrahydrofuran complexes of the metal borate include:

25 lithium tetrakis(pentafluorophenyl)borate, lithium tetrakis(phenyl) borate, lithium tetrakis(p-tolyl) borate, lithium tetrakis(m-tolyl) borate, lithium tetrakis(2,4-dimethylphenyl) borate, lithium tetrakis(3,5-dimethylphenyl) borate, lithium tetrafluoroborate, sodium tetrakis(pentafluorophenyl) borate, sodium tetrakis(phenyl) borate, sodium tetrakis(p-tolyl) borate, sodium tetrakis(m-tolyl) borate, sodium tetrakis(2,4-dimethylphenyl) borate, sodium tetrakis(3,5-dimethylphenyl) borate, sodium tetrafluoroborate, potassium tetrakis(pentafluorophenyl) borate, potassium tetrakis(phenyl) borate, potassium tetrakis(p-tolyl) borate, potassium tetrakis(m-tolyl) borate, potassium tetrakis(2,4-dimethylphenyl) borate, potassium tetrakis(3,5-dimethylphenyl) borate, potassium tetrafluoroborate, magnesium tetrakis(pentafluorophenyl) borate, magnesium tetrakis(phenyl) borate, magnesium tetrakis(p-tolyl) borate, magnesium tetrakis(m-tolyl) borate, magnesium tetrakis(2,4-dimethylphenyl) borate, magnesium tetrakis(3,5-dimethylphenyl) borate, magnesium tetrafluoroborate, calcium tetrakis(pentafluorophenyl) borate, calcium tetrakis(phenyl) borate, calcium tetrakis(p-tolyl) borate, calcium tetrakis(m-tolyl) borate, calcium tetrakis(2,4-dimethylphenyl) borate, calcium tetrakis(3,5-dimethylphenyl) borate, calcium tetrafluoroborate.

35 The specific examples of ether and tetrahydrofuran complexes of the metal aluminate include:

40 lithium tetrakis(pentafluorophenyl) aluminate, lithium tetrakis(phenyl) aluminate, lithium tetrakis(p-tolyl) aluminate, lithium tetrakis(m-tolyl) aluminate, lithium tetrakis(2,4-dimethylphenyl) aluminate, lithium tetrakis(3,5-dimethylphenyl) aluminate, lithium tetrafluoroaluminate, sodium tetrakis(pentafluorophenyl) aluminate, sodium tetrakis(phenyl) aluminate, sodium tetrakis(p-tolyl) aluminate, sodium tetrakis(m-tolyl) aluminate, sodium tetrakis(2,4-dimethylphenyl) aluminate, sodium tetrakis(3,5-dimethylphenyl) aluminate, sodium tetrafluoroaluminate, potassium tetrakis(pentafluorophenyl) aluminate, potassium tetrakis(phenyl) aluminate, potassium tetrakis(p-tolyl) aluminate, potassium tetrakis(m-tolyl) aluminate, potassium tetrakis(2,4-dimethylphenyl) aluminate, potassium tetrakis(3,5-dimethylphenyl) aluminate, potassium tetrafluoroaluminate, magnesium tetrakis(pentafluorophenyl) aluminate, magnesium tetrakis(phenyl) aluminate, magnesium tetrakis(p-tolyl) aluminate, magnesium tetrakis(m-tolyl) aluminate, magnesium tetrakis(2,4-dimethylphenyl) aluminate, magnesium tetrakis(3,5-dimethylphenyl) aluminate, magnesium tetrafluoroaluminate, calcium tetrakis(pentafluorophenyl) aluminate, calcium tetrakis(phenyl) aluminate, calcium tetrakis(p-tolyl) aluminate, calcium tetrakis(m-tolyl) aluminate, calcium tetrakis(2,4-dimethylphenyl) aluminate, calcium tetrakis(3,5-dimethylphenyl) aluminate, calcium tetrafluoroaluminate.

45 50 55 The catalyst of polymerization of olefin of the present invention can be prepared, for example, by mixing the metallocene compound (A) and the organoaluminum compound (B) with an olefin and subsequently bringing the resulting mixture into contact with the metal borate or aluminate (C). The molar ratio of the metallocene compound (A) to the metal borate or aluminate (C) is preferably in the range of from 1:0.01 to 1:1000, more preferably from 1:0.2 to 1:200, but is not specially limited thereto. The organoaluminum compound (B) is used preferably at a concentration in the

range of from 1×10^{-5} to 1×10^{-3} mol/l.

The olefin which is polymerizable in the present invention includes alpha-olefins such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, and 1-hexene; conjugated and unconjugated dienes such as butadiene, and 1,4-hexadiene; styrene; cyclic olefin such as cyclobutene; and so forth, and mixtures of two or more thereof.

5 The polymerization of olefin in the present invention may be conducted either in a liquid phase or in a gas phase. When the polymerization is conducted in a Liquid phase, any conventionally used organic solvent may be employed, the solvent including specifically benzene, toluene, xylene, pentane, hexane, methylene chloride, etc., or otherwise the olefin itself may be used as the solvent.

10 The catalyst of the present invention may be supported on an inert carrier. More specifically, the metallocene compound, the reaction product of the metallocene compound with the metal borate or aluminate, the reaction product of the metallocene compound with the organoaluminum compound, the metal borate or aluminate itself, or the organoaluminum compound itself may be supported on an inert carrier such as silica, alumina, magnesium chloride, a styrene-divinylbenzene copolymer, and polyethylene for use as the polymerization catalyst.

Such solid components obtained as above are particularly useful in gas phase polymerization.

15 The polymerization temperature is preferably in the range of from -100 to 230°C, but is not limited thereto.

The present invention is described in more detail by reference to examples without limiting the invention in any way.

20 The procedures of polymerization, reaction, and solvent purification were all conducted in an inert atmosphere. The solvent used in the reaction was purified, dried, and/or deoxidized preliminarily in a conventional method. The compounds used in the reactions were synthesized and identified in a conventional method.

Example 1

In a 2-liter autoclave, was placed 500 ml of toluene. Thereto 0.5 mmol of triisobutylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 0.5 μ mol of ethylenebis(indenyl)-zirconium dichloride, which had been synthesized by a known method, in 10 ml of toluene was added, and the mixture was stirred for 20 minutes. Thereto, 500 ml of propylene was charged, and stirred for 10 minutes. Further into the autoclave, 2.5 μ mol of diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate together with 10 ml of toluene was injected, and polymerization was allowed to proceed at 40°C for one hour. Consequently, isotactic polypropylene was obtained in a yield of 188 g.

Comparative Example 1

Propylene was polymerized in the same manner as in Example 1 except that 2.5 μ mol of dimethylanilinium tetrakis(pentafluorophenyl) borate was used in place of the diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate. Consequently, isotactic polypropylene was obtained in a yield of 45 g.

Example 2

In a 2-liter autoclave, was placed 500 ml of toluene. Thereto 0.5 mmol of triisobutylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 5 μ mol of isopropylidene(cyclopentadienyl-1-fluorenyl) zirconium dichloride, which had been synthesized by a known process, in 10 ml of toluene, was added, and the mixture was stirred for 20 minutes. Thereto, 500 ml of propylene was charged, and stirred for 10 minutes. Further into the autoclave, 25 μ mol of diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate together with 10 ml of toluene was injected, and polymerization was allowed to proceed at 40°C for one hour. Consequently, syndiotactic polypropylene was obtained in a yield of 110 g.

Comparative Example 2

Propylene was polymerized in the same manner as in Example 2 except that 25 μ mol of dimethylanilinium tetrakis(pentafluorophenyl) borate was used in place of the diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate. Consequently, syndiotactic polypropylene was obtained in a yield of 30 g.

Example 3

55 In a 2-liter autoclave, was placed 500 ml of toluene. Thereto 0.5 mmol of triisobutylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 0.5 μ mol of ethylenebis(indenyl)zirconiumdimethyl, which had been synthesized by a known method, in 10 ml of toluene was added, and the mixture was stirred for 20 minutes. Thereto, 500 ml of propylene was charged, and stirred for 10 minutes. Further into the autoclave, 2.5 μ mol

of diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate together with 10 ml of toluene was injected, and polymerization was allowed to proceed at 40°C for one hour. Consequently, isotactic polypropylene was obtained in a yield of 170 g.

5 Comparative Example 3

Propylene was polymerized in the same manner as in Example 3 except that 2.5 μ mol of dimethylanilinium tetrakis(pentafluorophenyl) borate was used in place of the diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate. Consequently, isotactic polypropylene was obtained in a yield of 40 g.

10 Example 4

In a 2-liter autoclave, was placed 500 ml of toluene. Thereto 0.5 mmol of triisobutylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 5 μ mol of isopropylidene(cyclopentadienyl-1-fluorenyl)zirconiumdimethyl, which had been synthesized by a known method, in 10 ml of toluene, was added, and the mixture was stirred for 20 minutes. Thereto, 500 ml of propylene was charged, and stirred for 10 minutes. Further into the autoclave, 25 μ mol of diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate together with 10 ml of toluene was injected, and polymerization was allowed to proceed at 40°C for one hour. Consequently, syndiotactic polypropylene was obtained in a yield of 95 g.

20 Comparative Example 4

Propylene was polymerized in the same manner as in Example 4 except that 25 μ mol of dimethylanilinium tetrakis(pentafluorophenyl) borate was used in place of the diethyl ether complex of lithium tetrakis(pentafluorophenyl) borate. Consequently, syndiotactic polypropylene was obtained in a yield of 25 g.

Example 5

In a 2-liter autoclave, was placed 500 ml of toluene. Thereto 0.25 mmol of triisobutylaluminum was added, and the mixture was stirred for 10 minutes. To this solution, a solution of 0.25 μ mol of ethylenebis(indenyl)zirconium dichloride, which had been synthesized by a known method, in 10 ml of toluene was added, and the mixture was stirred for 20 minutes. Thereto, a solution of 1.25 μ mol of diethyl ether complex of lithium tetrakis(pentafluorophenyl) aluminate in 10 ml of toluene was added. The autoclave was pressurized with ethylene to a pressure of 8 kg/cm², and the content in the autoclave was stirred at 40°C for one hour to polymerize ethylene. Consequently, polyethylene was obtained in a yield of 110 g.

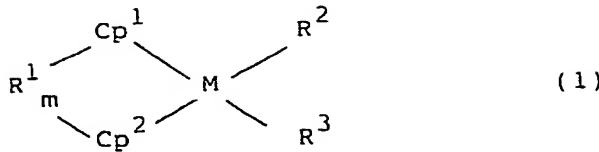
Comparative Example 5

Ethylene was polymerized in the same manner as in Example 5 except that 1.25 μ mol of dimethylanilinium tetrakis(pentafluorophenyl) aluminate was used in place of the diethyl ether complex of lithium tetrakis(pentafluorophenyl) aluminate. Consequently, polyethylene was obtained in a yield of 60 g.

As described above, with the catalyst and the olefin polymerization process of the present invention, the complicated synthesis steps are eliminated, and polyolefin having excellent properties and high moldability is produced efficiently.

45 Claims

1. A catalyst for polymerization, comprising (A) a metallocene compound, (B) an organoaluminum compound, and (C) a metal borate or a metal aluminate:
the metallocene compound (A) being represented by the general formula (1) below:



10 where Cp¹ and Cp² are independently a substituted or unsubstituted cyclopentadienyl group; R¹ is an alkylene group, an arylalkylene group, dialkylsilylene group, dialkylgermylene group, an alkylphosphinediyl group, or an alkylimino group having 1 to 20 carbons, R¹ crosslinking Cp¹ and Cp² together; m is 0 or 1; M is titanium, zirconium, or hafnium; and R² and R³ are independently hydrogen, halogen, or a hydrocarbon group, an alkoxy group, or an aryloxy group having 1 to 12 carbons,

15 the organic aluminum compound (B) being represented by the general formula (2) below:



20 where each R⁴ is independently hydrogen, an alkyl group, an alkoxy group, or an aryl group, at least one R⁴ being an alkyl group, and

25 the metal borate or the metal aluminate (C) being represented by the general formula (3):



30 where C is an alkali metal cation or an alkaline earth metal cation; L is a Lewis base; A is an anion having elemental boron or elemental aluminum; n is an integer of from 1 to 6; b and d are respectively an integer selected to balance the electric charge.

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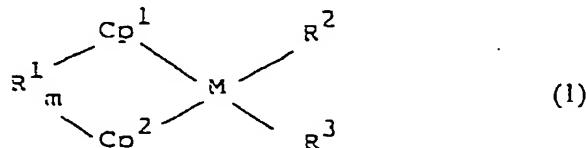
- 30 2. A catalyst according to claim 1, wherein the Lewis base L of general formula (3) is an ether compound or tetrahydrofuran.
3. A process of polymerization of olefin, wherein olefin is polymerized by using the catalyst according to any one of claims 1 to 2.

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Patentansprüche

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1. Katalysator für die Polymerisation, umfassend (A) eine Metallocen-Verbindung, (B) eine Organoaluminium-Verbindung und (C) ein Metallborat oder ein Metallaluminat: wobei die Metallocen-Verbindung (A) durch die nachstehende allgemeine Formel (1) wiedergegeben wird:



50 in der Cp¹ und Cp² unabhängig voneinander für einen substituierten oder unsubstituierten Cyclopentadienylrest stehend R¹ ein Alkylenrest, ein Arylalkylenrest, ein Dialkylsilylenrest, Dialkylgermylenrest, ein Alkylphosphindiylerest oder ein Alkyliminorest mit 1 bis 20 Kohlenstoffatomen ist, wobei R¹ die Reste Cp¹ und Cp² miteinander verknüpft; m 0 oder 1 ist; M ein Titan-, Zirkonium- oder Hafniumatom ist; und R² und R³ unabhängig voneinander für ein Wasserstoffatom, ein Halogenatom oder einen Kohlenwasserstoffrest, einen Alkoxyrest oder einen Aryloxyrest mit 1 bis 12 Kohlenstoffatomen stehen;

55 die organische Aluminium-Verbindung (B) durch die nachstehende allgemeine Formel (2) wiedergegeben wird:



5 in der jeder der Reste R^4 unabhängig voneinander für ein Wasserstoffatom, einen Alkylrest, einen Alkoxyrest oder einen Arylrest steht, wobei mindestens ein Rest R^4 ein Alkylrest ist; und das Metallborat oder das Metallaluminat (C) durch die allgemeine Formel (3) wiedergegeben wird:



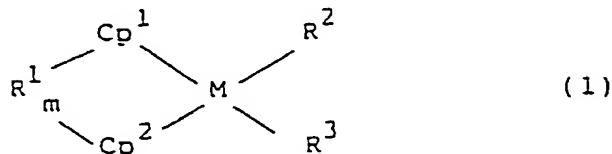
10 in der C ein Alkalimetallkation oder ein Erdalkalimetallkation ist; L eine Lewisbase ist; A ein Anion mit elementarem Bor oder elementarem Aluminium ist; n eine ganze Zahl von 1 bis 6 ist; b beziehungsweise d ganze Zahlen sind, die so gewählt sind, daß sie die elektrische Ladung ausgleichen.

15 2. Katalysator nach Anspruch 1, wobei die Lewisbase L in der allgemeinen Formel (3) eine Etherverbindung oder Tetrahydrofuran ist.

3. Verfahren zur Olefinpolymerisation, in welchem ein Olefin unter Verwendung des Katalysators nach einem der Ansprüche 1 bis 2 polymerisiert wird.

Revendications

25 1. Catalyseur pour la polymérisation comprenant (A) un composé de métallocène, (B) un composé d'organoaluminium, et (C) un borate de métal ou un aluminate de métal:
le composé de métallocène (A) étant représenté par la formule générale (1) ci-dessous:



40 où Cp^1 et Cp^2 sont indépendamment un groupe cyclopentadiényle substitué ou non substitué; R^1 est un groupe alkylène, un groupe arylalkylène, un groupe dialkylsilylène, un groupe dialkylgermylène, un groupe alkylphosphinediyle, ou un groupe alkylimino ayant 1 à 20 carbones, R^1 étant lié en même temps à Cp^1 et Cp^2 ; m est égal à 0 ou 1; M est le titane, le zirconium ou le hafnium; et R^2 et R^3 sont indépendamment un hydrogène, un halogène ou un groupe hydrocarbure, un groupe alcoxy, ou un groupe aryloxy ayant 1 à 12 carbones, le composé organoaluminium (B) étant représenté par la formule générale (2) ci-dessous:



45 où chaque R^4 est indépendamment un hydrogène, un groupe alkyle, un groupe alcoxy, ou un groupe aryle, au moins un R^4 étant un groupe alkyle, et le borate de métal ou l'aluminate de métal (C) étant représenté par la formule générale (3):



50 où C est un cation de métal alcalin ou un cation de métal alcalino-terreux; L est une base de Lewis; A est un anion ayant du bore élémentaire ou de l'aluminium élémentaire; n est un nombre entier de 1 à 6; b et d sont respectivement un nombre entier choisi pour équilibrer la charge électrique.

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2. Catalyseur selon la revendication 1, dans lequel la base de Lewis L de formule générale (3) est un composé d'éther ou un tétrahydrofurane.
3. Procédé de polymérisation d'oléfine, dans lequel une oléfine est polymérisée en utilisant le catalyseur selon l'une quelconque des revendications 1 à 2.

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